

## Kinetics of Formation and Absorption Cross Sections of the ClO Dimer

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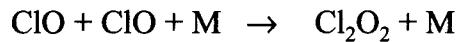
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## Motivation

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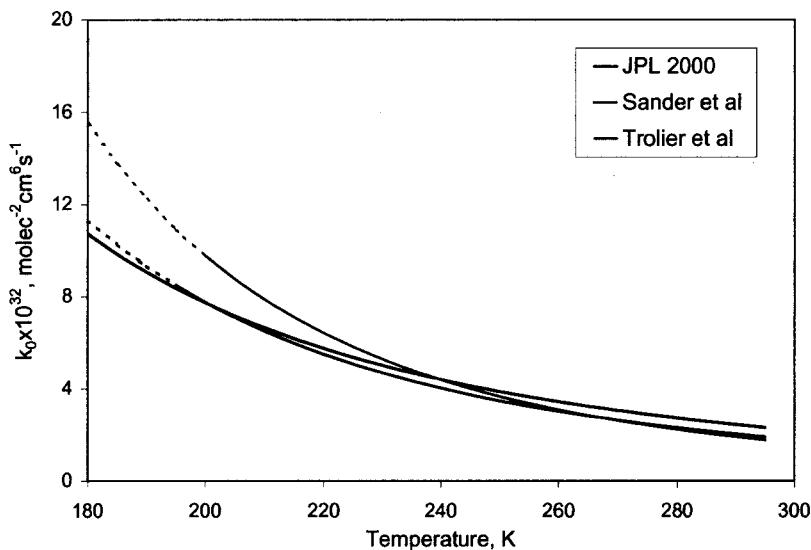


- $k_1$  and  $\sigma(\text{Cl}_2\text{O}_2)$  (and  $\Phi_{\text{Cl}}$ ) essential to quantify polar stratospheric  $\text{O}_3$  loss
- Measured and modelled Arctic spring  $\text{O}_3$  loss do not agree...

## Literature $k_0$ as $f(T)$

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(M = N<sub>2</sub>)



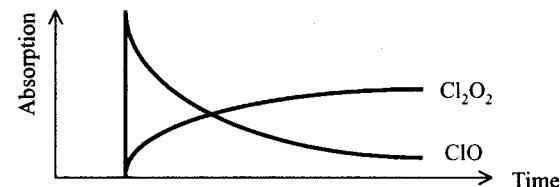
Dashed line = extrapolation below lowest T studied

No measurements below 195K...

## This work...

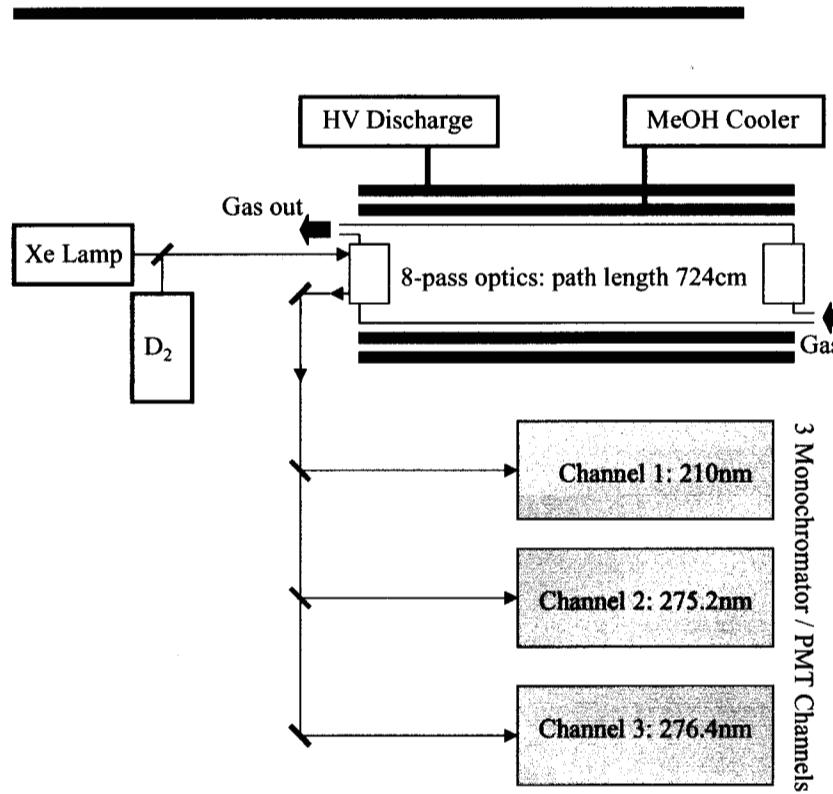
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- Flash photolysis / UV absorption study
- *Simultaneous* monitoring of ClO and Cl<sub>2</sub>O<sub>2</sub>

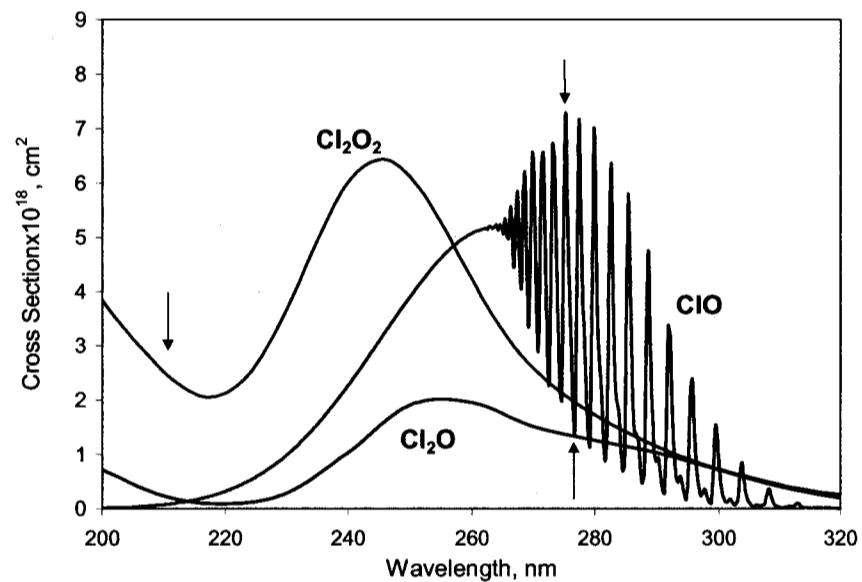


- Obtain  $k(ClO + ClO)$  from ClO decay
- Obtain  $\sigma(Cl_2O_2)$  or yield of Cl<sub>2</sub>O<sub>2</sub> (using literature  $\sigma$ )
- Temperatures down to 183K so far...

## Experimental System



## Monitoring Wavelengths

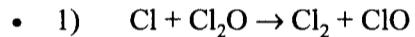


Monitor  $\text{ClO}$  via differential absorption (275.2, 276.4) and  $\text{Cl}_2\text{O}_2$  via absorption change at 210nm

## ClO Cross Sections

- Differential ClO cross section ( $\sigma_d$ ) dependent upon Temperature, Resolution, Wavelength

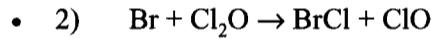
⇒ Measure  $\sigma_d(\text{ClO})$  for our system; two independent measurements performed:



Monitor  $\text{Cl}_2\text{O}$  loss at 255nm:

$$\Delta\text{Abs}_{255} = [\text{ClO}]_{t=0} L \{ \sigma(\text{ClO}) - \sigma(\text{Cl}_2\text{O}) \}$$

$\sigma(\text{ClO}, 255\text{nm})$  smooth (⇒ resolution independent) and T-independent

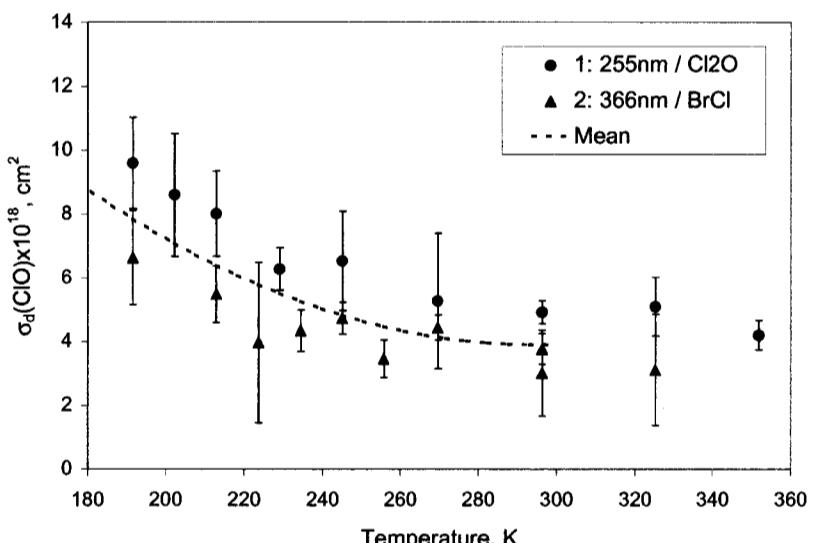


Monitor BrCl formation at 366nm:

$$\Delta\text{Abs}_{366} = [\text{ClO}]_{t=0} L \{ \sigma(\text{BrCl}) - \frac{1}{2}\sigma(\text{Br}_2) \}$$

Obtain  $\sigma_d(\text{ClO})$  as f(T)...

## $\sigma_d(\text{ClO})$ as f(T)

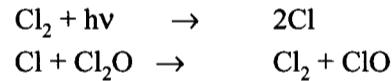


0.3nm FWHM

## Experimental Conditions...

- Radical Generation:

Broadband photolysis of  $\text{Cl}_2/\text{Cl}_2\text{O}/\text{N}_2$



- Concentrations:

$$[\text{Cl}_2] = (1-5) \times 10^{15} \text{ molec/cm}^3$$

$$[\text{Cl}_2\text{O}] = (1-2) \times 10^{14} \text{ molec/cm}^3$$

- Conditions:

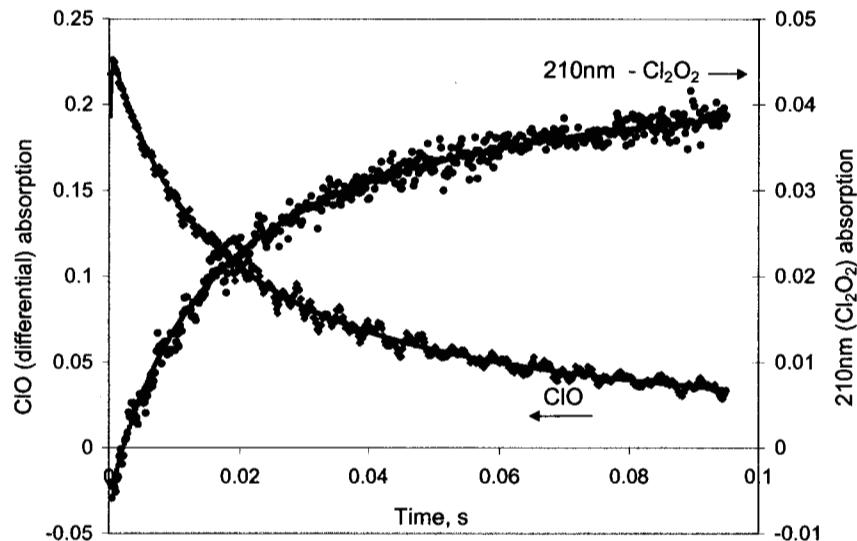
Pressure: 15-740 Torr

Temperature: 183 - 245K (gas flow)

- Obtain ClO and 210nm Absorption traces...

## Decay Traces & Fits

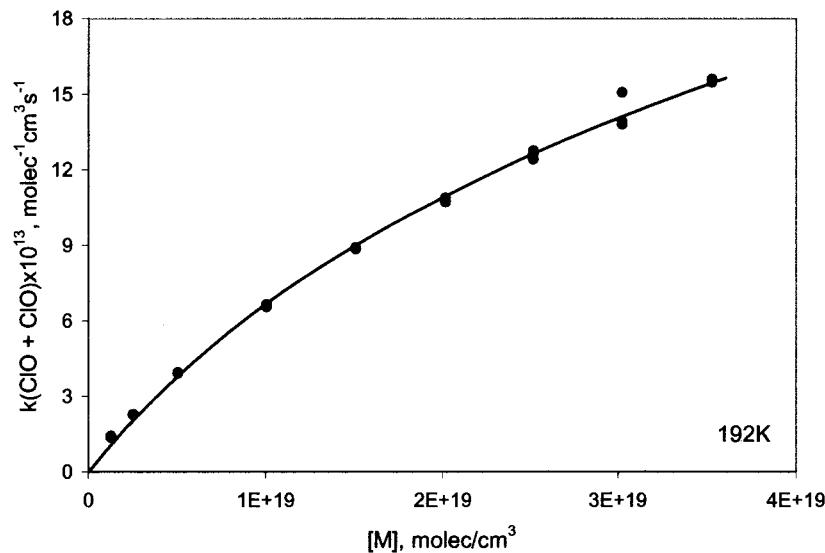
203K, 300 Torr



Optimise       $[\text{Cl}]_{t=0}$   
                   $k(\text{ClO} + \text{ClO})$   
                   $\sigma(\text{Cl}_2\text{O}_2)$

## Fall-off analysis

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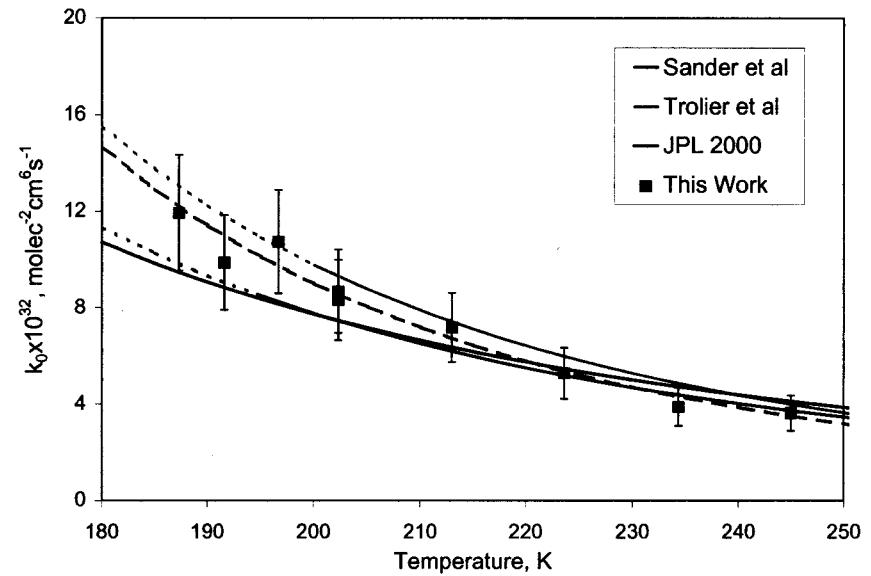


$$k = \frac{k_o [M]}{1 + (k_o [M]/k_\infty)} \times 0.6^{(1 + [\log(k_o [M]/k_\infty)])^2 - 1}$$

Obtain  $k_o, k_\infty$  as  $f(T)$ ...

## $k_o$ as $f(T)$ ...

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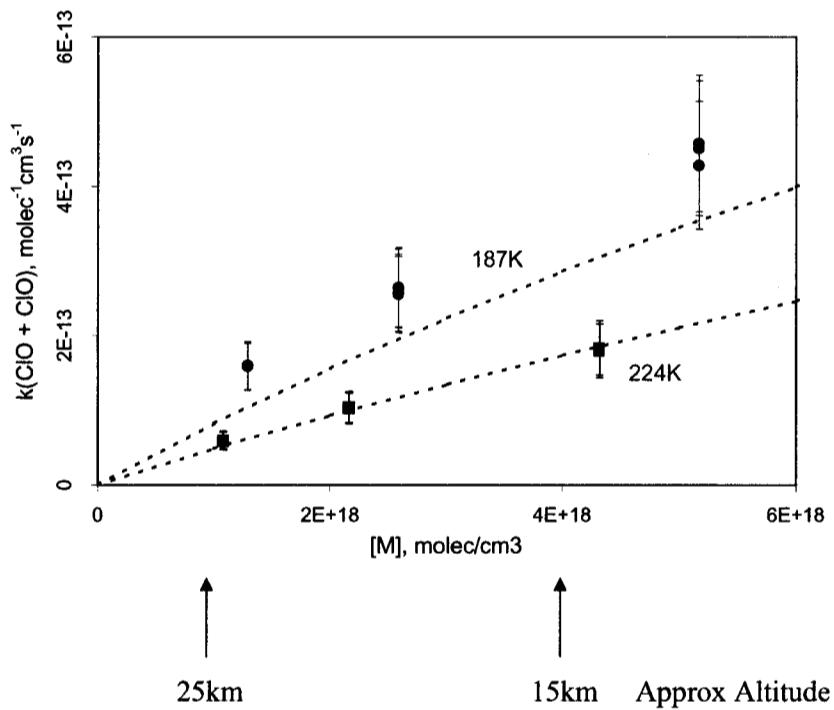


Dotted lines = extrapolation below lowest T studied

$$k_o = 1.37 \times 10^{32} \times (T/300)^{-4.64}$$

## Stratospheric conditions:

This work (data points) vs. NASA Recommendation (line) at 187 and 224K



## Results

- ClO + ClO Kinetics:

$$k_0 = k_0(300) \times (T/300)^{-n} \quad (T < 250\text{K})$$

	This Work	Evaluation
$k_0(300) \times 10^{32}$	$1.37 \pm 0.38$	2.2
n	$4.64 \pm 0.67$	3.1

( Evaluation = JPL / NASA Data Evaluation 2000 )

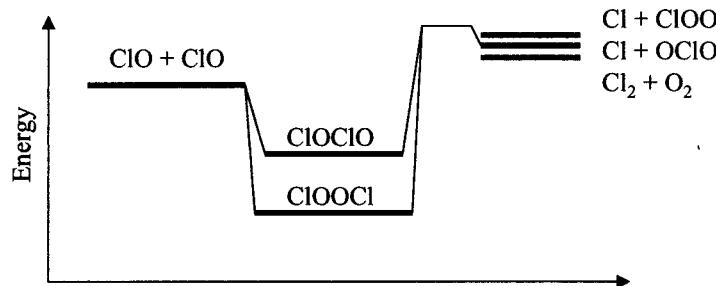
$$k_\infty = (1.47 \pm 0.81) \times 10^{-12} \times (T/300)^{-3.4 \pm 1.2}$$

- Dimer Cross-Section:

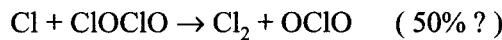
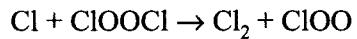
$$\sigma(\text{Cl}_2\text{O}_2), 210\text{nm} = (2.5 \pm 0.5) \times 10^{-18} \text{ cm}^{-2}$$

- JPL/NASA:  $2.52 \times 10^{-18} \text{ cm}^{-2}$

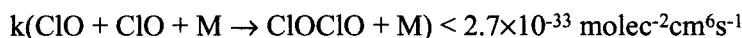
## Stability of ClOClO at low T ?



- Perform experiments under slight excess Cl atoms; look for OCLO formation: (195K)



- Saw no OCLO...



or ≈ 7% of ClO + ClO (195K)

But complex system: Cl + OCLO, ClO + OCLO and



## Conclusions

- $k(\text{ClO} + \text{ClO})$  higher at very low temperatures than extrapolation of previous results suggests
- $\sigma(\text{Cl}_2\text{O}_2), 210\text{nm}$  in agreement (within precision) with current recommendation
- No evidence for stable ClOClO at low T
- Future work:

Refine determination of  $\sigma_d(\text{ClO})$

Extend measurements of lower T: 180K ?

Improve  $\sigma(\text{Cl}_2\text{O}_2)$  S:N; Measure  $\sigma(\text{Cl}_2\text{O}_2)$  at other  $\lambda$